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Nanofiltration Process Efficiency in Water Desalination

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Abstract: Nanofiltration (NF) membranes have applications in several areas. One of the main applications has been in brackish and sea water treatment for drinking water production as well as for wastewater treatment. NF can either be used to treat all kinds of water including ground, surface, and wastewater or used as a pre treatment for desalination. The introduction of NF as a pre treatment is considered a breakthrough for the desalination process. NF membranes have the ability to remove turbidity, hardness, fluoride and nitrate as well as a significant fraction of dissolved salts. Desalination can be performed with a significantly lower operating pressure and becomes a much more energy-efficient process. NF membrane transport properties, process prediction and modeling are very important. The ability to predict the performance of NF processes will allow for a reduce number of experiments, saving money and helping to understand the NF separation mechanisms. Several studies have investigated the partial and selective demineralization induced by NF. New methods were suggested to minimize and to control the brine disposal in brackish and sea water treatment. The paper will also address the application of NF for water treatment and as a pre-treatment step for low energy consumption processes such as photovoltaic-powered units.

Keywords: Nanofiltration, brackish water, sea water, desalination

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INTRODUCTION

Membrane science and technology are now the dominant technology in water desalination for the solution of the problem of potable water deficiency in various parts of the world (1). According to the World Health Organization, more than 12,000 desalination plants are in operation throughout the world in 2005, producing about 40 million m^3 of water per day (2) (Fig. 1). These numbers are growing rapidly as the need for fresh water supplies grows more acute, technologies improve, and unit costs decrease. The 80 million m^3/day mark should be passed in 2008. It is recalled that the daily 2007 U.S. consumption per capita is 0.35 m^3/day (100 million m^3/day in the USA alone, www.worldwater-council.org).

Nanofiltration (NF) technologies are widely used for the production of safe drinking water, and for the recovery of reusable water from various industrial effluent streams. NF offers several advantages such as low operating pressure, high flux, high retention of multivalent anion salts and organic matter, relatively low investment and low operation and maintenance costs. Worldwide applications of NF have increased (3) because of these advantages. NF offers often a valuable alternative to reverse osmosis (RO), which requires a high operating pressure and energy cost. Thus, membranes with lower rejections of dissolved components, but with higher water permeability, would be a great improvement for separation technology. The research efforts on reverse osmosis membranes have had a major impact on all of the progress in nanofiltration science and technology. Evaporation plants have been

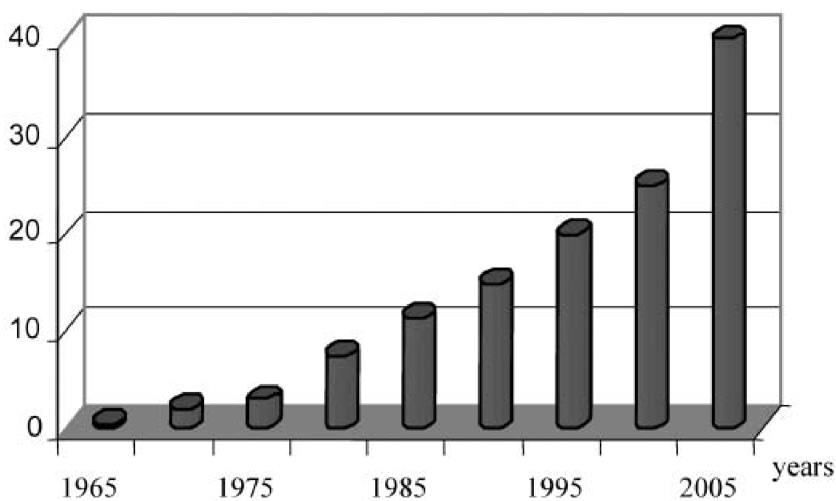

Figure 1. Evolution of desalination plants efficiency over the world.

replaced by RO systems in operation all over the world for desalination processes (4). The easy engineering and the relatively low energy consumption by RO membranes, compared to evaporation, is one of the reasons for this success. In seawater desalting, in fact, the global energy consumption of RO, with a recovery factor of 30% and energy recovery, has been 5.32 kWh/m^3 corresponding to a primary energy consumption of 60 kJ/kg (5).

Costs for brackish water desalination are 60–70% lower than those for seawater desalination. RO desalination is not only devoted to the production of drinkable water but today is also strategic in various industrial sectors and particularly in ultra pure water production for the electronic industry (6, 7).

Water in many areas of the world is scarce and of poor quality. In some areas high levels of treatment are required either due to contamination or to high salinity. Nanofiltration and low-pressure reverse osmosis membranes are well-recognized technologies to treat waters of qualities ranging from low salinity surface water to high salinity seawater. In remote communities the operation of such facilities may be limited by the availability of electricity. Solar, or photovoltaic, energy is the ideal source of renewable energy to overcome this problem. Considering the various options for a small system designed to deliver a permeate flow of 400–1000 liters per day from brackish wells, the most suitable membrane for salt retention was selected and the pump energy requirements calculated (8).

Membrane science and technology has led to significant innovation in both processes and products over the last few decades, offering interesting opportunities in the design, rationalization, and optimization of innovative production processes (9). The most interesting development for industrial membrane technology depends on the capability to integrate various membrane operations in the same industrial cycle, with overall important benefits in product quality, plant compactness, environmental impact, and energetic aspects (10, 11). The case of transportation technologies is of particular interest. The purpose here is to summarize the extent to which nanofiltration membrane processes have been integrated into industrial practice. Some of the most interesting results already achieved in nanofiltration engineering will be presented, and predictions about future developments and the possible impact of new membrane science and technology on sustainable industrial growth will be analyzed.

NANOFILTRATION TRANSPORT PROPERTIES

Because of the growing interest in nanofltration for industrial use, a better insight in the retention mechanisms in nanofiltration is needed. It will make it possible to understand membrane performances for specific applications (12) (Fig. 2). Understanding nanofiltration transport mechanisms is essential for making progress in optimizing membrane separation technology (13–16).

The complexity of the transfer mechanisms makes the prediction of membrane performance extremely difficult in charged nanoporous membranes. Indeed, the pore-level description in charged porous media is usually provided by the space charge model (SCM) (18–24). Recent work employing sophisticated statistical mechanical methods suggests that this model, or suitable extensions thereof, should also be valid in nanopores. In the case of sufficiently weak membrane charge and tight pores, the SCM can be approximated by a homogeneous electrotransport model comprising the mesoscopic extended Nernst-Planck (ENP) equations and local charge electroneutrality. The mesoscopic homogeneous model can be obtained from the pore-level SCM using 3-D volume-averaging techniques that do not require a simple capillary structure at the pore length scale and are therefore useful even for nanofilters exhibiting complicated morphologies.

A computer simulation program, Nanoflux, has been developed in Lefebvre et al. (25) laboratory to solve the homogeneous electrotransport model for up to eleven ionic species using numerical methods. To gain a deeper understanding of NF transport and validate Nanoflux numerical calculations, an analytical approach appeared to be essential (26).

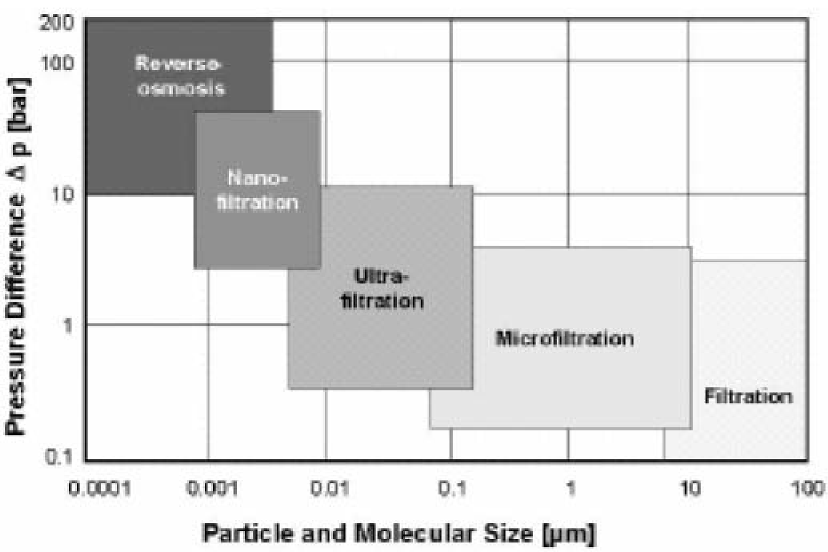

Figure 2. Separation capabilities of pressure driven membrane separation [adapted from 17].

Transport properties of a tubular nanofilter with amphoteric properties have been investigated by means of the steric electric and dielectric exclusion homogeneous model (27, 28). Within the scope of this 1D model, the separation of solutes results from transport effects (described by means of extended Nernst-Planck equations) and interfacial phenomena including steric hindrance, the Donnan effect, and dielectric exclusion. The effective volume charge density of the membrane has been determined from tangential streaming potential experiments coupled with conductance experiments in a potassium chloride solution at various pH values ranging from 2 to 11. This model based on the hindered extended Nernst-Planck and Stokes equations solve the transport equations within the scope of the hindered electro transport (HET) model, which takes into account ion charge and size (rejection is controlled by both electrostatic and steric effects) (29). The calculations using both an analytical solution to the classic ENP model, which neglects the ion size, and numerical methods via the NF simulation program, Nanoflux, was also validate.

Bowen et al. (30) were the first to coin the term "Donnan-steric-pore model" (DSPM) that was a modified form of a hybrid model which is based on the extended Nernst-Planck equation with a Donnan condition at the membrane/solution interfaces and the hindered nature of transport in the membranes. The model takes into account the hindrance effects for diffusion and convections to allow for transport of ions/charged solutes taking place within a confined space inside the membranes. Subsequent studies (31, 32) showed that the model can very well predict the rejection performance of single salt solutions. Recently, Bowen and Wellfoot (33) suggested modifications to the DSPM models for NF membranes. The first modification was used to take into account the effects of log-normal pore size distributions on the rejection of uncharged solutes and NaC1 at hypothetical NF membranes (34–37).

Another approach for NF modeling is through the Spiegler-Kedem model (38–41). This black-box approach allows the membranes to be characterized in terms of salt permeability, Ps, and the reflection coefficient σ. This model is in the first instance limited to binary salt systems, and in the limiting case to a binary salt system with a complete rejection of organic ion (39, 41).

Diawara et al. (42) used an NF45 membrane to treat highly fluorinated brackish water. Their approach was based on the phenomenological model of Spiegler, Kedem and Katchalsky (SKK) (43, 44) under dilute solution conditions but neglected the charges carried by the membrane. Experimental results showed for the first time that selective defluorination can be achieved with a NF membrane. The rejection was around 96% (42). Furthermore, following the permeate salt concentration versus the reverse of the permeate flux, it was possible to developed a very simple method. The method was able to quantify separately both parts of the mass transfer occurring in NF: convection and/or solution–diffusion.

Ben-David et al. (45) studied the important role of partitioning in the removal of organics by NF membranes. It is noted that strong partitioning in polyamide membrane negatively affects the rejection of organic contaminants in RO and NF filtration. The effect may be significant for larger contaminants having low solubility in water. In extreme cases this may counterbalance the sieving effect and limit the applicability of RO/NF to the removal of moderately hydrophobic substances (e.g., hormones, nonyl phenol, etc). The hydrophobicity of polyamides is good for salt rejection, yet it may be unfavorable with the removal of organics. To date, the main effort has been directed towards optimal membranes for desalination, but a more diverse range of membranes (e.g., in terms of polarity) might be desirable to achieve optimal rejection for different classes of organics (46). Ionic partitioning at the interfaces between the membrane and the external phases takes into account three separation mechanisms, which are steric hindrance, Donnan equilibrium and dielectric exclusion. The screening of dielectric exclusion is introduced by the presence of other ions. Consequently, a fixed electric charge is created, which causes additional screening (47).The dielectric constant variation that arises between the aqueous solution in the pores and that of the membrane material is presumed to be critical in determining the rejection mechanism deriving from the dielectric effects.

Zeta potential measurements were used to calculate the surface charge of some nanofiltration membranes and establish the rejection modeling. The zeta potential as well as the calculated surface charge increased with increasing salt concentration in the bulk. An empirical approach was proposed to incorporate the change of the dielectric constant between the bulk and pore solution and calculate the ion distribution (48).

IONIC COMPONENTS FROM BRACKISH AND SEA WATER

The NF process becomes increasingly important for large scale NF applications in the drinking water production and treatment. One main reason for large scale applications of RO membranes is that the commercial simulation software for the RO process has been very mature, such as RO design (Hydranautics, USA), ROSA (DOW, USA) and Toray RO (Toray, Japan). The simulation software helps consumers save large numbers of preliminary experiments, but it cannot be applied to design the "Loose RO" process, that is NF process, since the effect of salt concentration is not considered (49, 50).

The effects of species and concentration of salts on the separation performance of NF membranes showed that, for most salts, rejection rate by ESNA 1 membrane decreased with the rise in concentration. This is an unusual result since salt permeability would generally increase with the growth of concentration. This phenomenon is commonly explained by the fact that the effective area of the membrane pore becomes larger due to a smaller thickness of the electrical double layer. The presence of a permanent charge in the membrane matrix allows for increased electrostatic repulsive forces throughout the entire pH range (51). For the different valence ions, the anionic rejection sequence and the cationic rejection sequence at 10 mol/m^3 concentration can be explained by the Donnan exclusion theory, which suggests that for a single-salt solution, a higher valence co-ion caused a higher ion rejection, whereas a higher valence counter-ion leads to a lower rejection of the salt. For the same valence ions, the rejection sequence could be affected by the difference in ion diffusivities, i.e., an ion is retained more if it has a smaller diffusivity. However, Da-Xin Wang et al. (52) have shown that magnesium and calcium salts have a constant rejection rate by ESNA 1 and they justified this exception by the fact that Stokes radii of Mg^{2+} and Ca^{2+} are larger than those of NH_4^+, Na^+, K^+, Cl^-, NO_3^- and SO_4^{2-}; the change of the effective area of the membrane pore can hardly affect the solute permeability for magnesium and calcium salts.

Fluoride Removal

Fluoride concentration in drinking water is very important for human health. Optimal fluoride content is within the range of 0.5–1.0 mg/L (51). Excess fluoride in drinking water is responsible for stained teeth and/or bones diseases (Fig. 3).

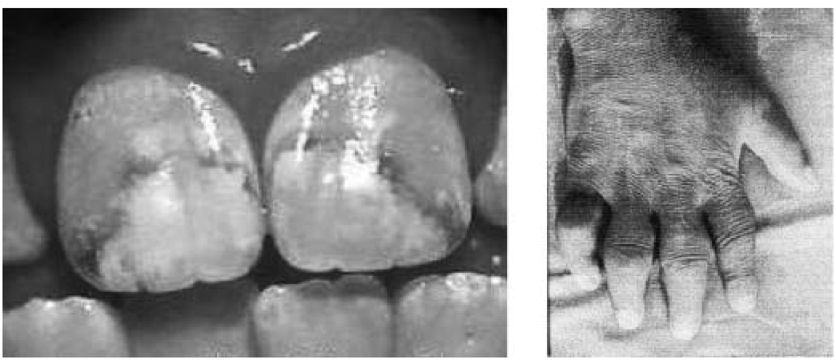

Figure 3. Dental coloration and bone deformation due to fluorosis (adapted from 53).

Nanofiltration (NF) membrane performance on fluoride removal from high fluoride content water was systematically investigated (54). The membranes used are negatively charged commercial thin-film composite (TFC) membranes (DS-5-DL, DS-51-HL and SR-1). The membrane performance was interpreted in terms of membrane parameters: pure water permeability (L_P), pore radius (r_P) and constant surface electrical potential (ψ). The parameters were obtained by fitting the 100 and 1000 ppm single salt (NaF) experimental data to a mathematical model that was developed based on the extended Nernst–Planck equation and the Graham equation. The experimental results indicated that the rejection of NaF increased with the applied pressure. The solution flux also increased as soon as the feed concentration decreasing while applied pressure increasing. The experimental data were compared with the model developed. The model was also used to predict the membrane performance at 20 and 2000 ppm NaF solutions (54).

One possibility to treat high fluorinated brackish drinking water using nanofiltration membranes has been improved with an approach based on the phenomenological model of Spiegler, Kedem and Katchalsky (SKK). The phenomenological parameters σ (the membrane reflection coefficient) and P_s (the solute permeability) are calculated and it appears that σ can be linked linearly to the hydration energy of the halide ions. Furthermore, P_s appeared to be linked to the type of electrolyte. The σ values are highly dependent on the anion present in the salty solutions. NF generally used for elimination of divalent ions, describes its potential to selectively separate the following single halide salts: NaF, NaCl, NaI, LiF and LiCl. It was observed for the first time that a selective defluorination can occur using a NF membrane.

The investigation of fluoride removal from various solutions (NaF, NaCl, $NaNO_3$, and Na_2SO_4) by using three commercial nanofiltration membranes denoted NF70 (Filmtec), DESAL5 DL (Osmonics), and MT08 (PCI) under 8 bars, 293 K in batch recirculation mode is also improved (55). The membranes were tested for their rejection potential of fluoride ions in the presence of chloride, nitrate and sulfate ions. Fluoride rejection efficiency ranges from 78% to 95%. The improved efficiency of the nanofiltration membranes is closely linked to the nature of the solution. The high rejection level (above 98%) of the divalent sulfate ions (50 or 200 mg/L) gives rise to the Donnan effect (56). In brackish water conditions, for all the membranes, there was a noticeable influence of anion size and hydration. The membrane hydraulic performances remain high and stable; this is a good answer towards enquiring about how to select a membrane for water application (57).

Nitrates Removal

The problem of water pollution by nitrate ions is observed in numerous countries in Africa, quite particularly in semi urban environments where the purification networks are mostly non-existent. Drinking waters taken directly from the well present contents in nitrates commonly reaching $200\,mg.L^{-1}$ (58) greatly exceeding $50\,mg.L^{-1}$ the level recommended by the world health organization for drinking water. Regarding MPS44 and DESAL membranes of nanofiltration, nitrate ions retention is here always lower than that of chlorides, which itself is generally weaker than that of fluoride ions. This difference of selectivity between monovalent anions can be attributed to hydration differences (59). With a [$NaNO_3$] solution, the membrane–solution interactions are strong and they favour nitrate retention. With [$NaNO_3$, NaCl] mixtures, the shielding of the membrane charge is important and nitrates retention decreases sharply. With [$NaNO_3$, NaCl, NaF] mixtures, where only $5\,mg.L^{-1}$ of NaF were added to the [$NaNO_3$, NaCl] mixture, the shielding effect alone cannot explain the strong decrease observed. Similarly, small additions of sulfate ions to the [$NaNO_3$, NaCl] mixture leads to a dramatic decrease of nitrates retention (60).

Quémeneur et al. established the critical effect of the cation hydration energy on the nitrate retention with a variety of NF membranes (61). It also gives information on the membrane-solute and solute-solute interactions on the retention of nitrates. Table 1 lists the effectiveness of the NF270 nanofiltration in the treatment of natural water polluted by nitrates associated with different cations.

It should be noted that an increase in concentration of any divalent anion affects particularly the retention of nitrates, whereas that of a divalent cation tends to improve it. However, in the same study, Quémeneur et al. showed that the effect of a divalent cation can be balanced by a monovalent cation. Table 2 shows the changes in nitrate

Table 1. Retention of the nitrate anion according to the nature and the hydration energy of the associated cation $\Delta P = 7$ bars and $C(NO_3^-)$ $100\,mg.L^{-1}$ (61)

Associated cation	Hydration energy of cation, $kJ.mol^{-1}$	Nitrate retention %
NH_4^+	320	49
Na^+	407	51
Ca^{2+}	1584	63
Cd^{2+}	1815	71
Cu^{2+}	2105	76

Table 2. Retention of the nitrate ions according to the composition in cations for a fixed concentration of nitrates of 200 mg.L^{-1} and at 7 bars of applied pressure (61)

Solution composition		Nitrate retention %
$Ca(NO_3)_2$ %	Na NO_3 %	
25	75	16.7
50	50	90.6
75	25	34.5

retention when a 200 mg.L^{-1} nitrate solution made with different mono- and divalent cations and passed through a NF270 membrane (61).

Santafé-Moros et al. (62) showed that NF270 gave very high flux but very low nitrate rejection, even at the lowest concentrations in the feed. NF90 and ESNA1-LF membranes produced a rejection high enough to obtain good water quality. Additionally, they carried out an experimental design to determine the effect of pH. The pH is a very influential factor; however, the membranes presented different performance. Important differences were observed in the membrane performance when comparing the model solutions results with those of the groundwater. This confirms the convenience of experimental tests on pilot plant with the groundwater to be treated in order to select the most adequate membrane. Thus, one can infer that the application of nanofiltration technology is useful to produce drinking-water from brackish water with a nitrate ion concentration below 150 mg. L^{-1} (62, 63).

Hardness and Other Divalent Cation Removal

Many brackish water and wells water locations exhibit a content of monovalent salts; e.g., for NaCl that is low enough to satisfy drinking water requirements, but the hardness is too high for adequate distribution and use. NF can selectively reduce the hardness removing the contributing salts, much like a conventional water softener, but without the need for regeneration.

In order to predict NF membrane performance, a systematic study on the filtration performance of selected commercial NF membranes against brackish water and seawater is required. Three commercial nanofiltration membranes (NF90, NF270, NF30) have been used to treat highly concentrated (NaCl) salt solutions up to 25,000 ppm, a salinity level similar to that of seawater. For a salinity of 5000 ppm and a pressure of 9 bars, the experimental results showed that NF90 could achieve a salt rejection up to 95% producing potable water with about 250 ppm NaCl (64). However, the NF90 rejection dropped to 41% at a salinity of

25,000 ppm and the same 9 bars pressure. Rejection levels achieved by NF270 were between 11–29%, while NF30 gave the lowest rejection in the range of 3–6% (64).

Nanofiltration is a very effective process for hardness removal. Using the UTC20 membrane, retentions higher than 90% were found for multivalent ions, whereas monovalent ions were retained for about 60–70%. A rejection of 94% was found for calcium, remaining constant at higher recoveries. The effect of temperature and recovery on the permeate flux could be described by expressing flux as a function of water viscosity and net pressure difference (65–67). Highly sulfated, hard water from a flooded iron mine was treated by nanofiltration for the production of drinking water. The first industrial-size installation (125 m^3/h) was started in 1993 at the Mery sur Oise site, near Paris in France. The treatment goals were the reduction of the biodegradable dissolved organic carbon levels to values limiting bacterial growth within the network as well as the reduction of atrazine and simazine levels, and water hardness. Since then, two other installations Jarny and Batilly plants have been put into service in the East of France, near the city of Metz, capital of the Lorraine country. These two plants were built in order to solve an issue specific to Lorraine, where the closing and the shutdown of the mining drainage systems had caused an increase in the salinity levels of water resources (68).

Dinà Afonso et al. (69) found that for a given set of operating conditions, the salt rejections rates follow the order: $R_{MgCl2} < R_{MgSO4} < R_{Na2SO4}$; they argued that the anion valence and the feed concentration of the salt rejections, typical of electrically charged membranes, were qualitatively in agreement with the ion exclusion principle. Using the same argument, Schaep et al. (70) found the retention sequence below: $LaCl_3 > MgCl_2 > NaCl$ for NF40 and CA30 membranes of nanofiltration.

Walha et al. (71) associated high temperatures (800°C) to NF to reduce the hardness (42.5% of Ca^{2+}, 38.3% of Mg^{2+} and 67.1% of SO_4^{2-}) of brackish water from Gabes and Zarzis cities (south of Tunisia). Hardness removal from a lake in Taiwan has been studied by Yeh et al. and cited by Hilal et al. (72), who relied on different methods such as a conventional filtration process followed by ozone treatment, granular activated carbon and pellet softening, and an integrated membrane process (UF/NF) and compared to the conventional process. Softening was achieved by all processes, but water produced by membrane filtration yielded the best quality, as measured by turbidity (0.03 NTU), total hardness rejection (90%), and dissolved organics rejection (75%) (72). Visvanathan et al. (73) studied the effect of the presence of ions, operating pressure, feed, pH, and suspended solids on the rejection properties, and concluded that higher pressure and suspended solids content increase rejection, while rejections were somewhat lower at higher ionic strength. They also concluded, in agreement with Hilal et al. (72), that both high and low pH of the feed water produced low rejection. Better rejection was found at a pH range of 7–9, suggesting that most brackish waters might not require a pH adjustment.

Metallic Ion Removal

Cadmium is one of the main toxic pollutants generated by industrial activities and many methods have been used to remove it from wastewater created by these industries (74). Removal of cadmium Cd^{2+} ions from aqueous streams has been investigated through a nanofiltration membrane process. The retention was studied as a function of the counterion nature, ionic strength and pH. The convective and diffusive parts of the mass transfer quantification, allows understanding the transport through the membrane which can be described by irreversible thermodynamics. The Speigler-Kedem model can be applied in order to determine phenomenological parameters of the membrane and the solute permeability of ions (74).

Industrialization and urbanization are often associated to large pollution emissions of Zinc and its alloys mostly used in mechanical engineering and construction. To figth this toxic pollution, very strict standards were imposed for heavy metal content in water. The maximum zinc concentration allowable in tap water must below 5 ppm (5 mg/L) in the French regulation (law-regulation 89–3 modified 2003) (75). The level will be lowered to 2 ppm in 2008. NF results have shown that Zn^{2+} ion retention increases with pressure and reaches a maximum of 90% which varies slightly with the concentration. These observed retention values for zinc have been found better than retention obtained with copper or cadmium (40%) (74, 75).

Removal from water of other metallic ions such as indium (In^{3+}) and hexavalent chromium was investigated via nanofiltration technology as a possible alternative to the conventional methods used for aqueous solution. Rejection measurements with a single reference salt revealed that Donnan exclusion plays an important role. The rejection rate depends on the ionic strength and pH as it decreases with greater ionic strength. It rises at higher (basic) pH (76, 77).

NANOFILTRATION AS PRE-TREATMENT FOR DESALINATION

The role of the pre-treatment is to purify seawater to a quality acceptable by RO membranes as seen with the biggest seawater reverse osmosis plant of Tajura in Libya. The plant is designed to produce high quality drinking water and industrial water (78).

NF is used in drinking water production in several other areas than for pre-treatment in connection with seawater desalination. NF was used for the first time by Hassan et al. (79) as pre-treatment for seawater reverse osmosis (SWRO) and multistage flash (MSF) processes. In these integrated processes, NF minimized hardness, microorganisms and turbidity. At a pressure of 22 bars, NF removed hardness due to the ions Ca^{2+}, Mg^{2+}, $SO_4{}^{2-}$ and $HCO_3{}^{-}$. It reduced the total respective hardness by 89.6%, 94.0%, 97.8%, 76.6% and 93.3%. In addition, NF reduced the monovalent ions concentrations of Na^{+}, and K^{+}; each ion was rejected by 40.3% and overall seawater total dissolved solids (TDS) by 57.7%, while the total hardness was removed by 93.3%. The permeate thus obtained was far superior to seawater as a feed to SWRO or MSF. This made it possible to operate a SWRO and MSF pilot plant at a high recovery: 70% and 80%, respectively. The integration of NF with MSF processes makes it possible to operate MSF plants at a high distillation temperature of 120°C to 160°C with high distillate recovery, and again without chemical addition. These integrated desalination systems, combined with a reduction of chemicals and energy, allows producing fresh water from seawater at a 30% lower cost compared to conventional SWRO (80, 81).

Eriksson et al. (82) indicate that NF is used as a pretreatment step for a seawater RO plant at Umm Lujj, Saudi Arabia, where the nanofiltration pre-treatment step reduces total hardness from 7500 to 220 ppm, TDS from 45,500 to 28,200 ppm, and chloride from 21,600 to 16,400 ppm. With the ionic make up at the Umm Lujj plant, sulfate was rejected at a rate better than 99%, magnesium at 98%, calcium at 92% and bicarbonate at 44%. The remaining ionic content was below 2 ppm for sulfate, 29 ppm for magnesium, 40 ppm for calcium and 17 ppm for bicarbonate. This NF unit was composed of 27 housings in parallel, each with 6 DK8040F elements, and was installed in September 2000, as a pre-treatment step for the RO unit. The 360 m^3/h seawater feed was delivered to the NF unit at 25 bars gauge pressure with a 65% permeate recovery and resulted in 234 m^3/h NF permeate that was fed into the existing RO unit. The NF unit reduced the permeate TDS and allowed the RO unit to produce 130 m^3/h permeate with a conductivity at 25°C of 600 μS/cm. Then, it appears clearly that NF as pre-treatment for seawater RO could be economical in cases where the RO unit experiences excessive membrane fouling and gives a too high permeate TDS value. One of the major advantages is that an additional 25% high quality water can be produced using the same total number of membrane elements and with a pressure reduced by 17%. The GE-OK nanofiltration membranes have proved to be excellent for pre-treatment of seawater, both in front of RO units and/or evaporation. Before large scale testing was performed by the Saline Water Conversion Corporation (SWCC) in Saudi Arabia at the

Umm Lujj seawater reverse osmosis plant, it was argued that the scaling problem would be transferred from the reverse osmosis membrane to the nanofiltration membrane (83).

Nanofiltration filters as pre-treatment unit operations for both thermal and membrane seawater desalination processes have helped reduce the amount of chemicals, as well as lower the energy consumption and water production cost, thus leading to more environmentally friendly practices.

A quality feed pre-treatment process is instrumental to successful operation of a water treatment plant. With the proper pre-treatment, fouling potential of the feed water can be reduced and produce an increased lifetime for the membranes. However, performance of media filtration, which has been the conventional pre-treatment technique for many years, is still lacking in many aspects. Intensive consumption of chemicals and inconsistency in performance are some of the main disadvantages of media-filtration. With the nation's push towards more self-reliance in fresh water supply at an affordable cost, there is an imperative need to look for alternative pre-treatment techniques and improve process reliability (84–86). AI-Sheikh et al. (87) relied on this idea to reason that the effect of the pre-treatment on SWRO plants was very pronounced. Thus, an adequate pre-treatment design should yield optimized productivity and extend the membrane operation life. This will significantly decrease all operating costs.

NANOFILTRATION AS BRINE DISPOSAL TECHNIQUE

NF for brackish water treatment or for seawater pre-treatment represents today one of the most widespread practice. Despite this success, specific actions are required in order to solve problems related to water recovery factors, brine disposal, cost and quality of the produced water (88). Clean water and concentrate reject products are generated by desalination plants. Concentrates generally may contain up to 20% of the treated water. Brine is a concentrate stream that contains a TDS concentration greater than 36,000 ppm (36 g/L). Critical concentrate parameters are TDS, temperature, and specific weight. It is now recognize that cost-effective and environmentally sensitive concentrate management as the most significant obstacle to the widespread use of desalination technologies. Proper concentrate disposal and construction methods incorporated in the plant's design can minimized the concentrate impact on the receiving water environments and groundwater aquifers. The influence of several parameters on the economical feasibility of the whole process must be taken into account such as the dissolved salts concentration and quantity of dissolved CO_2 for the correct choice of NF membrane which is of vital importance (89–91).

Nanofiltration has been successfully applied to the recovery of spent anion exchange brines because polymeric nanofiltration membranes have ionizable carboxyl and amine functional groups. They tend to carry a negative surface charge at neutral pH, which actively rejects multivalent anions such as colored charged anions, phosphates and citrates (92). Experiments on brine concentration, using commercially available nanofiltration membranes have shown that rejection was adversely affected by high brine concentration and elevated cationic concentrations due to charge shielding of the membrane. However, it is already demonstrated that nanofiltration can be utilized to recycle spent cation exchange brines. The experiments confirmed that membrane surface charge could be manipulated by lowering the pH below the membrane iso-electric point to make it positive (Fig. 4). So the recommendations for nanofiltration recycling of spent cation exchange brine are based on pH adjustment with HCl to less than pH=3.

It is also important to minimize brine concentration for minimizing shielding effect. Fouling of NF membranes is typically caused by natural organic and inorganic materials that adhere to surface and pores of the membrane. The result is obviously a deterioration of efficiency. There are several factors that can affect the cleaning process, which include temperature, pH, concentration of the cleaning chemicals, contact time between the chemical solution and the membrane and the operation conditions such as the cross-flow velocity and pressure. The topic of nanofiltration membrane cleaning and performance regeneration is occasionally discussed in the literature but more resources should be dedicated to this research area (93). An acceptable desalination plant is expected to meet environmental regulations; be cost-effective, according

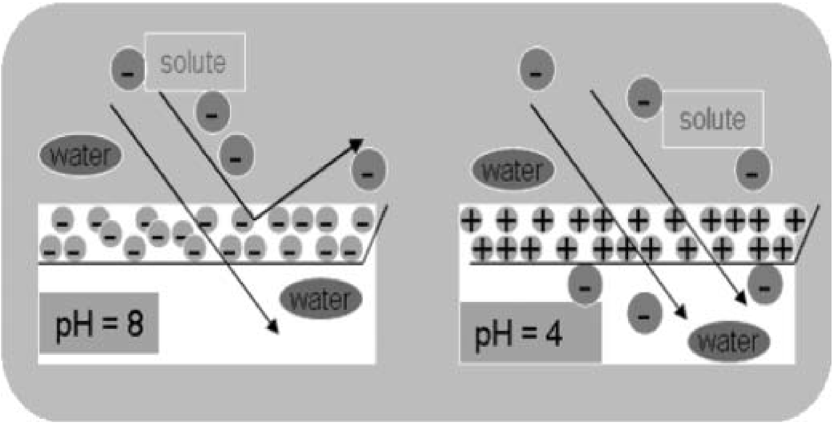

Figure 4. Example of TiO_2 membrane behavior according the pH of the solution (with an iso electric point = 6).

to Maurel (94) in terms of construction, operation and management, as well as for the costs associated with monitoring and permit fees (95, 96).

RENEWABLE ENERGY FOR MORE EFFICIENCY

In remote communities the operation of NF and/or RO facilities may be limited by the availability of electricity. Solar, or photovoltaic, energy appear to be the ideal source of renewable energy to overcome this problem as seen in Australia (97). A water purification system has been developed in Australia which combines a hybrid ultrafiltration and reverse NF/RO system with a solar energy unit (98). Richards et al. (99) report on the successful field testing of a photovoltaic powered desalination system. Their system is intended for use in remote areas of the Australian outback, where fresh water is extremely limited and it is often necessary to drink high salinity bore water. The optimum operating pressure when filtering bore water was determined to be in the range 6–7 bars. The disinfected and desalinated drinking water depends on the salinity of the feed water and the system operating conditions. Then the specific energy consumption ranged from 2 to 8 kWh/m^3 (99).

Water desalination technologies and their possible coupling with solar energy are of particular interest, especially for countries having vast arid and isolated areas with limited access to electricity derived from the national power grid. Economic factors being one of the main barriers to the expansion of solar technology so far, as described by Fiorenza et al. (100–102), the water production cost was estimated for RO and multiple effect distillation, each one powered by solar thermal and solar photovoltaic energy, respectively. Data obtained for plants with a capacity ranging from 500 to 5000 m^3/day were compared to those of a conventional desalination system. In addition, the influence of various parameters, such as depreciation factor, modules cost and oil price, was also considered.

CONCLUSION

Desalinating brackish groundwater can represent an important alternative resource for water utilities. High-pressure membranes that use reverse osmosis and nanofiltration are recognized as viable desalination technologies. Although several membranes are available on the market, there is no universal and systematic protocol for evaluating their performance. Developing such a protocol will allow utilities to standardize membrane-screening procedures, which ultimately benefits the manufacturers as well as the utilities.

A comprehensive review is given (1) for the use of NF membranes in water and wastewater treatment, (2) NF separation mechanisms, (3) ionic components removal from brackish and sea water, (4) use of brine disposal, and (5) renewable energy for NF efficiency. In addition, NF was used as a pre-treatment step in the desalination process. It was shown that NF membranes can be used to treat water by removing hardness, dissolved fluoride, nitrate and other metal ions. The enhanced rejection of divalent cations confirms that acidic conditions induce a positive charge on the membrane below the iso-electric point of the membrane (pH 4), causing Donnan exclusion of multivalent cations. The divalent calcium and magnesium are retained, while monovalent like sodium and potassium permeate through the membrane to maintain electroneutrality. NF separation mechanism is mostly attributed to charge and steric effects taking place across the membrane thickness.

Indeed, one may conclude that nanofiltration is one of the most powerful water treatment processes when the membranes and operating conditions are carefully chosen. This filtration process exhibits critical attractive features such as: ease of operation, reliability, comparatively low energy consumption level, and a high efficiency of pollutant removal.

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